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INVESTIGATION OF SINGLE CRYSTAL
FERRITE THIN FILM
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by

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SUMMARY

The deposition effort has been devoted to experiments utilizing FeCl_3 in place of FeCl_2 with the goal of achieving an improved match to the reactivity of the LiI. Considerable difficulty was encountered in achieving and maintaining reproducible FeCl_3 reactivity and transport rates. Evaluation of the best deposits obtained with this material indicated that a reactivity imbalance still remained. Consequently the decision has been made to return to FeCl_2 as the iron source material.

Analysis of previous deposits made with FeCl_2 has provided additional insight into the mechanisms responsible for low magnetization, conductivity, optical absorption and ferromagnetic relaxation in the films.

Comparison of the relevant material properties shows that good quality epitaxial LiFe_5O_8 on MgO or MgAl_2O_4 has definite advantages over $\text{Y}_3\text{Fe}_5\text{O}_{12}$ on $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ in the launch and propagation of surface and volume acoustic waves. The realization of these advantages requires the achievement of resonance linewidths comparable to the best bulk values.

INTRODUCTION

This research program has as its goal the growth and characterization of single crystal thin films of lithium ferrite (LiFe_5O_8). Such films have potential applications in the emerging microwave surface acoustic wave technology. The method of growth has been chemical vapor deposition onto an MgO substrate.

The initial portion of the program was devoted to the determination of feasibility of CVD as the growth process and to the establishment of the proper deposition conditions (Ref. 1). During this interval it was determined that the zonal behavior characteristic of successful CVD of other magnetic oxides was also attainable with the Li-Fe oxide system.

At the start of the second year, the characterization effort was greatly expanded in order to identify and evaluate the films and the results of various changes in the deposition conditions. The joint deposition-characterization effort produced considerable improvement in the quality and characteristics of the deposits during the second year (Ref. 2). It was verified that epitaxial $\alpha\text{-LiFe}_5\text{O}_8$ had been successfully deposited. However, two major problems remained: 1) the deposits contained excess iron and thus were not stoichiometric and 2) the surface quality was rather poor. It was felt that both the non-stoichiometry and the poor surface quality were traceable to the difficulty in optimizing the deposition conditions due to the imbalance between the reactivities of the Li and Fe source materials. In an attempt to remedy this situation, FeCl_3 was substituted for FeCl_2 as the iron source material. Most of the work during this report interval has been devoted to deposition experiments with the $\text{FeCl}_3\text{-LiI}$ system. Analysis

of previous deposits was continued in order to further characterize the properties of these films. The most promising deposits from the FeCl_3 work have also been evaluated.

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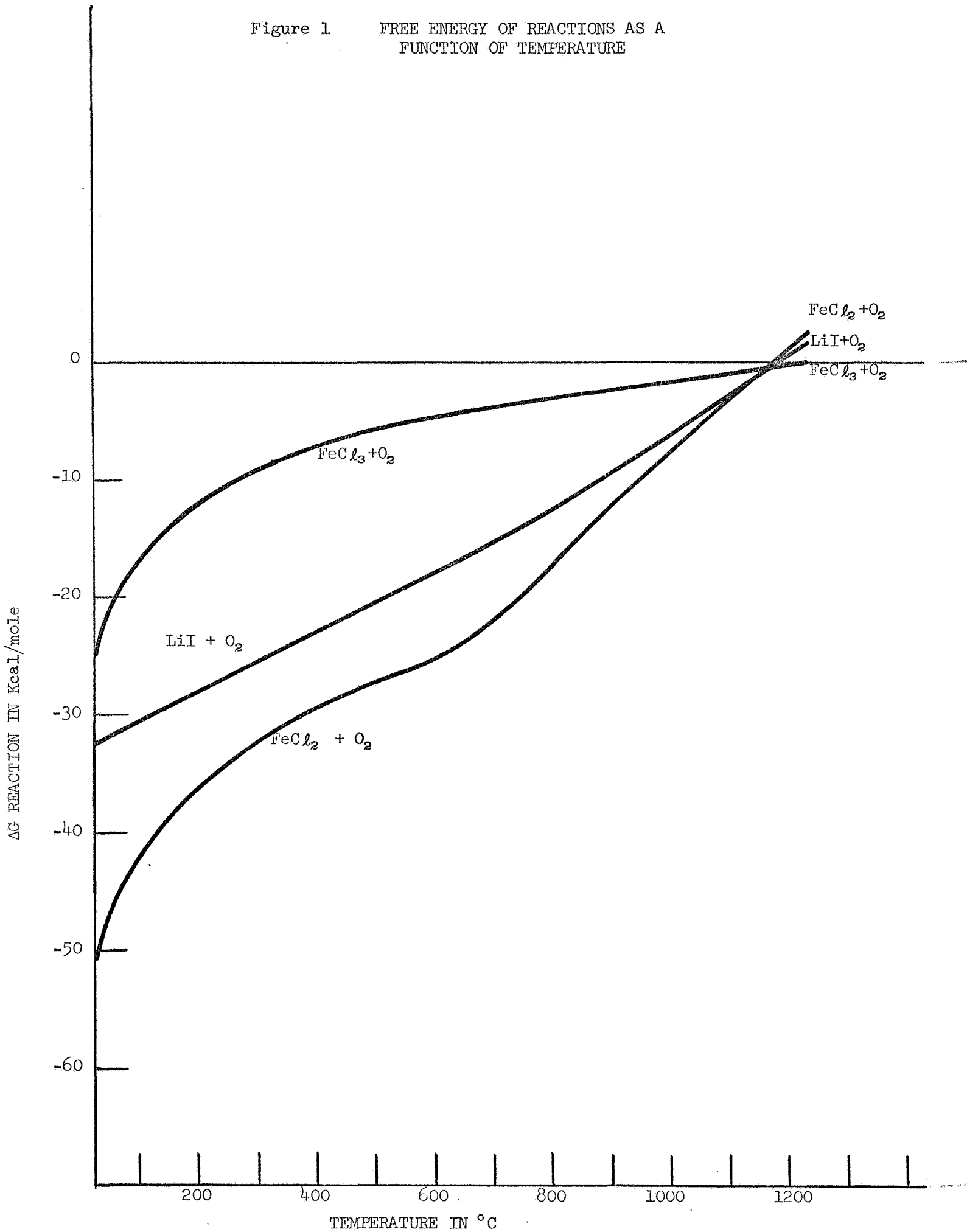
EXPERIMENTAL APPROACH AND PROGRESS

Deposition

Most of the deposition effort during this interval has been devoted to experiments with the goal of replacing ferrous chloride with ferric chloride to obtain a better match to the lithium iodide reactivity. The relative reactivities of various Li and Fe halides and the basis for the selection of the LiI-FeCl₂ combination were discussed in the First Interim Report (Ref. 1). The use of ferric halides was not considered at that time because previous experience in epitaxial deposition had demonstrated the advantages of the ferrous material with regard to purity, ease of fabrication and reproducibility. In other deposition programs the source material reactivity differences either were not as critical or could be controlled by introducing certain reaction products into the incoming gas flow to suppress the reactivity of one material. This type of control has been attempted in the Li ferrite runs by adding HCl to the vertical gas flow but success has been rather limited.

The free energy of reaction with O₂ is shown as a function of temperature for LiI, FeCl₂ and FeCl₃ in Figure 1. It can be seen that at 900°C the reactivity of FeCl₂ is greater than that of LiI. However, the problem is compounded by the fact that when both vapors are simultaneously present in the deposition zone the reactivity of the lithium halide is reduced while that of the iron is not (Ref. 1). This leads to an even greater imbalance in the reactivities. However, in the FeCl₃-LiI system at 900°C this interaction effect presumably produces a change in the direction of an improved match in reactivities.

Figure 1 FREE ENERGY OF REACTIONS AS A FUNCTION OF TEMPERATURE



Commercially available anhydrous FeCl_3 has been utilized as the iron source material. Because of its relatively low purity compared to the internally prepared FeCl_2 , it is sublimed and recondensed before use. A residue invariably remains after the commercial material has been sublimed, indicating a relatively low initial purity. Unfortunately, samples of FeCl_3 purchased in various grades of purity from different vendors do not appear to be significantly different in this respect as judged by the amount of residue. An additional complication in the use of FeCl_3 is that its sublimation temperature is below its melting point and transport occurs by sublimation from the powder form rather than by evaporation from the liquid as is the case with FeCl_2 . This large surface area in the powder form causes severe problems in obtaining and maintaining constant transport rates.

It was first thought the low sublimation temperature of ferric chloride ($\sim 300^\circ\text{C}$) would preclude its use inside the reactor where it would be positioned 18 inches from the 950°C LiI source zone. Consequently, preliminary runs were made with the FeCl_3 outside of the actual reactor. In this series of runs it was verified that the FeCl_3 could be reacted with oxygen both alone and with the simultaneous reaction of LiI . These experiments, however, emphasized the desirability of having both source materials inside the reactor. The main problem resulting from having the FeCl_3 outside the "T" reactor was the heat loss in the tubing between the source cup and the "T" inlet. This resulted in condensation of the FeCl_3 in the tubing and the lower portion of the vertical tube of the "T". It was subsequently established that the source heater controls and zone isolation in the reactor were adequate to allow placing the FeCl_3 in the "T" without having excessively high Fe transport rates. The FeCl_3 transport rate can be varied from 1.5 to 12 grams/hr with the present reactor setup. It has been necessary to increase the O_2 flow to 3.0 cfh when using the ferric chloride to obtain adequate reactivity of this material.

After the FeCl_3 source cup was placed inside the reactor several runs were made in which both Fe and Li were transported into the reaction zone. The deposits were translucent red, magnetic and generally polycrystalline. The growth rate in these runs was quite high, 0.5 to 1.0 micron per minute, and the deposition zones were typically three to four inches long. A primary cause of the rapid growth rate in these preliminary depositions was that the FeCl_3 transport rate was considerably higher than that of the LiI. The transport rates of the FeCl_3 in terms of the source temperature and the flow rates were measured and the Fe transport was reduced while holding the Li constant in an attempt to get close to the proper ratio.

In the course of the experiments attempting to establish the optimum growth conditions we encountered serious problems in maintaining and reproducing deposition conditions from run to run. The main problem has been lack of reproducible FeCl_3 transport and reactivity. To correct the former a four-inch shell heater was added at the bottom of the vertical chamber of the reactor. This gave a longer flat temperature zone in the FeCl_3 source area. Some improvement was observed but the Fe transport rates remained difficult to reproduce.

Although the transport control was still not adequate, a series of promising deposits were obtained from Runs 453, 454, 455 and 457. Two important facts emerged from these runs. First, fairly smooth (111) deposits and pyramidal (100) deposits grew side by side (i.e. both seeds in the same zone). Thus, the FeCl_3 -LiI system is like the FeCl_2 -LiI system and it was not necessary to identify new film growth peculiarities. Second, the total deposition zone was quite long (~ 4 inches). This was one of the goals in changing to FeCl_3 . The longer total zone should mean that the Fe:Li ratio

will be more nearly constant across a substrate. This is necessary to obtain the pure LiFe_5O_8 . Following these encouraging results it was anticipated that adjustments could be made to improve the deposits, characterize them and make final adjustments to optimize the LiFe_5O_8 zone. The deposition conditions of Run 455 are shown in Table I.

TABLE I
DEPOSITION CONDITIONS - RUN 455

Vertical Gas Flow	He = 22 cfh
	HCl = 0.08 cfh
Gas Injected Directly Into LiI Cup	He = 1.5 cfh
Horizontal Gas Flow	He = 2 cfh
	O ₂ = 3 cfh
LiI Transport Rate	7.5 gm/hr
FeCl ₃ Transport Rate	9.4 gm/hr
Seed Temperature	895°C
LiI Source Temperature	930C
FeCl ₃ Source Temperature	335°C
Substrates	Cleaved (100) and Polished (111) MgO

However, the deposition behavior following Run 457 was again erratic. Shortly thereafter the fused silica "T" broke. Since the reactor was supposed to be moved into a different room at the earliest convenient time, we chose this time to move.

During the moving period an appraisal of the FeCl_3 results led to the decision to return to FeCl_2 as the iron source material. The FeCl_3 was simply not reproducible enough in its transport and reactivity behavior. This is probably due to a combination of variable purity and the large surface area from which transport takes place by sublimation. These experimental disadvantages appear to outweigh the hoped-for advantage due to the improved reactivity match to LiI.

Another factor in the decision is that the initial characterization of the deposits made with FeCl_3 indicates that they are probably similar to some of the early low magnetization films obtained with the ferrous material. Thus we are apparently still iron-rich but are probably oxidizing the iron completely due to the increased O_2 flow and thus obtain mixtures of LiFe_5O_8 and $\alpha\text{-Fe}_2\text{O}_3$. More FeCl_3 experiments may be attempted at some later date, but only when there are sufficient lithium ferrite films available for the desired evaluation work.

After a few trial runs with the FeCl_2 , using cleaved (100) seeds, we were back to the deposition conditions which had produced the best films to date. Unfortunately, the quartz "T" broke just as depositions were to be attempted on polished (111) seeds. During the conditioning period of the new "T" we are proceeding with the characterization of the best deposits obtained using FeCl_3 for comparison with those obtained from FeCl_2 .

It is intended to resume depositions as soon as the new "T" reactor tube is conditioned. These runs will utilize FeCl_2 as the iron source material unless the evaluation of films made with FeCl_3 reveals some decided improvement

over earlier deposits. The plan is to return to those conditions which have produced the most promising deposits, i.e. runs in the 375-379 series. From this point we will seek to optimize conditions by a combination of minor deposition excursions and evaluation of the resulting deposits. Modifications in the reactor during the FeCl_3 work have improved the temperature control, source temperature zone flatness and zone isolation. These changes should allow better control and reproducibility of future deposits.

Thermodynamic calculations similar to those reported by Wehmeier (Ref. 3) for YIG transport are being extended to the lithium ferrite CVD. It is anticipated that these will allow prediction of the effect of certain changes in deposition conditions and provide insight into changes required to overcome the past and present deposition problems.

Characterization

Chemical analysis.--The composition of certain deposits has been determined by wet chemical analysis and by electron beam microprobe. During this period of the program we have analyzed some low magnetization deposits from the FeCl_2 runs, samples from the best FeCl_3 runs, and a flux-grown crystal.

Three of the low magnetization deposits 262Z1, 262Z2.5 and 371Z1.5 were selected to undergo substrate removal, X-ray studies and wet chemical analysis. In the two samples from Run 262 the detached deposit consisted of two apparently different materials, uneven black particles and translucent brown sheets. The black particles appeared to be considerably more magnetic than the brown flakes. In 262Z1 the brown material remained relatively intact while in 262Z2.5 it broke up into many small particles. Separation of the two materials was performed in 262Z1 and they were submitted individually to wet chemical analysis. Sample 262Z2.5 was analyzed without any such separation. The detached film 371Z1.5 did not show this dual nature. Portions of the deposits 453Z3, 455Z1B and 455Z3, which were made with FeCl_3 , were also submitted to wet chemical analysis. The results are shown in Table II.

TABLE II
CHEMICAL ANALYSIS OF DEPOSITS

<u>Sample</u>	<u>Fe (micrograms)</u>	<u>Li (micrograms)</u>
262Z1A-Black Particles	36.2	3.8
262Z1B-Brown Sheets	60.4	<0.1*
262Z2.5-Mixture	20.0	8.0
371Z1.5	140.9	<0.1*
453Z3	328.8	2.0
455Z1B	432.1	2.1
455Z3	445.5	4.0

*This value is the limit of detection of Li

The data on the samples from Runs 262 and 455 shows that the Fe:Li ratio of a deposit decreases as one moves downstream in the reactor (i.e. to higher zone numbers). This is typical of the zone behavior of the CVD process in a "T" reactor, and reflects the higher reactivity of the Fe source material. The deposits made with $FeCl_3$ are quite high in iron indicating that the anticipated proper balance of reactivities and transport rates was not achieved in these runs.

The absence (or very low level) of lithium in 371Z1.5 indicates that it was too far upstream under the deposition conditions of this run. The results on the samples from Run 262 show that some older films consist of two distinctly different materials. Thus one must be cautious in interpreting the characterization data on early samples since it may represent only an average of two quite different components. Microscopic observation of many of these old films indicates that the smooth brown Fe-rich layer was probably between the substrate and the black material.

Portions of Samples 261Z1A, 261Z1B and 371Z1.5 have been submitted for Mg analysis but the results are not yet available.

Electron beam microprobe analysis was performed on a portion of a flux-grown crystal. Care was taken to avoid areas of inclusions but a uniform concentration of Pb was detected in the sample. The uncorrected X-ray intensity line for Pb in the sample is one per cent of the intensity of that from the 5-9's Pb standard. This would typically place the weight of Pb in the sample in the 0.5 to 2.0 per cent range. Wet chemical analysis confirmed the presence of Pb and gave the following cation weights.

Fe:	106.8 micrograms
Li:	2.4 micrograms
Pb:	31.2 micrograms

X-ray analysis.--Powder patterns were attempted on the two materials from 262Z1 and on 371Z1.5. Good patterns were obtained from the black particles, 262Z1A and from 371Z1.5. To obtain a pattern from these minute samples it is necessary to place them on the outside of a capillary tube and position the tube so that the sample is in the X-ray beam. Several attempts to obtain a pattern on 262Z1B were unsuccessful.

Because of the great similarity of the diffraction patterns of the various possible constituents of the films it is not always possible to unambiguously identify the deposit from the X-ray measurements. Based on the chemical analysis and the diffraction pattern of 262Z1A, it is concluded that this material is probably a mixture of LiFe_5O_8 and LiFeO_2 . The combined chemical and X-ray data on 371Z1.5 indicate that it is a mixture of $\alpha\text{-Fe}_2\text{O}_3$ and at least one cubic spinel phase, possibly MgFeO_4 and/or Fe_3O_4 .

Lattice constant measurements from the powder patterns and from diffractometer scans of deposits still attached to the MgO are shown in Table III.

TABLE III
LATTICE CONSTANTS OF EPITAXIAL DEPOSITS

<u>Sample</u>	<u>a_0</u>	<u>Technique</u>
262Z1B	8.334	Debye-Scherrer
371Z1.5	8.350	Debye-Scherrer
376Z1.5 (After Anneal)	8.330 8.307	Diffractometer Diffractometer
454Z2	8.318	Diffractometer
455Z1A	8.342	Diffractometer
455Z2	8.335	Diffractometer

As a check on the diffractometer method, the lattice constants of the MgO substrates were also determined and values from 4.211 to 4.215 were obtained on the various samples.

Magnetization.--Values of $4\pi M_s$ for the various deposits evaluated during this interval are listed in Table IV.

TABLE IV
MAGNETIZATION OF EPITAXIAL DEPOSITS

<u>Sample No.</u>	<u>$4\pi M_s$ (gauss)</u>
262Z1	1920
262Z2.5	2120
371Z1.5	2700
454Z2	1300
455Z2	2100

From the chemical and X-ray analysis it is apparent that some of the early low magnetization films such as 262Z1 consisted of two distinct layers having different magnetizations. Some of the later deposits such as 371Z1.5 contain little, if any, lithium and their low magnetizations probably result from a mixture of weakly and strongly magnetic phases such as α -Fe₂O₃, Fe₃O₄ and MgFe₂O₄. The magnetization values of the deposits made with FeCl₃ source material are very low. If they contain lithium ferrite it must be Mg-doped or must contain α -Fe₂O₃ as a second phase. The high iron content makes the latter seem more reasonable.

Resistivity.--The resistivity of deposits made with FeCl₃ has been determined by four point probe measurements. The values for films 455Z1A, 455Z2 and 454Z2 are 682, 158 and 460 Ω -cm respectively. These resistivities are higher than any previously obtained on deposits that had not been annealed in O₂ and indicate that the Fe²⁺ content of these films is lower than that of previous deposits. This was somewhat anticipated on the basis of the increased O₂ flow and of having the original source material in the ferric state. However, complete absence of ferrous iron should result in a resistivity value which is orders of magnitude higher than the best value quoted above. This is evident from the results of Kato (Ref. 4) and from our measurements on annealed deposits.

Optical absorption.--The transmission spectra of several deposits were obtained for correlation with other data. The spectra of the high magnetization deposits made from FeCl₂ source material usually show an absorption band at $\sim 1.5\mu$ which varies in intensity from sample to sample. This band was present in films 263Z1 and 375Z1.5 which were measured during this report period. Such deposits typically have resistivities in the 1 to 100 Ω -cm range.

As a result of annealing studies both the 1.5μ band and the low resistivity have been attributed to deviations from stoichiometry and the resulting presence of Fe^{2+} in the deposits (Ref. 2). Additional support for this assignment comes from spectra of deposits made from $FeCl_3$. These deposits have the highest pre-anneal resistivity yet obtained and 455Z1A and 454Z2 show no indication of the 1.5μ band while 455Z2 shows a slight hint of it. Interestingly, 379Z1.5 does not have a noticeable absorption at 1.5μ yet its resistivity is comparable to the other deposits which show a pronounced band. Hall effect measurements performed on this sample showed that the room temperature conductivity is determined by a 0.115 eV donor level rather than a ~ 0.8 eV (1.5μ) level. The strong MgO lattice absorption beginning at $\sim 8\mu$ prevents observation of the 0.115 eV (11μ) band in the optical spectrum. It has been reported in the literature (Ref. 5) that tetrahedrally coordinated Fe^{2+} has a strong absorption band centered on $\sim 1.9\mu$. Although Fe^{2+} prefers the octahedral site in inverted spinels it is possible that some may enter the tetrahedral sites and produce the band at $\sim 1.5\mu$. The existence of a level at 0.115 eV means that the room temperature resistivity is not dominated by the mechanism corresponding to the 1.5μ band. Thus the strength of this band is probably not a reliable indicator of the total resistivity or Fe^{2+} content.

Conduction mechanisms.---The resistivity and optical absorption data obtained in the previously reported annealing studies indicated that the low resistivity and the 1.5μ absorption band are due to the presence of Fe^{2+} . However, the mechanism of conduction was not investigated. In an attempt to gain further insight into the nature of the conduction in these deposits,

Hall effect measurements were performed on Sample 379Z1.5 over a limited temperature range, 25°C to 138°C. The Hall effect measurements determined that the deposit is n-type with $\rho = 69 \Omega\text{-cm}$. The carrier concentration is 3.6×10^{16} at 25°C with a mobility of $2.5 \text{ cm}^2/\text{v-sec}$ and an activation energy of 0.115 ev. Other investigators (Ref. 6, 7) have reported activation energies of this approximate value for $\text{Fe}^{2+}\text{-Fe}^{3+}$ electron exchange between octahedral sites in iron oxide compounds. Additionally Haberey (Ref. 6) has measured an activation energy of ~ 0.6 ev due to Fe^{2+} in hexagonal ferrites which he attributes to hopping between other than octahedral sites. Since the 1.5μ absorption band corresponds to an energy of ~ 0.8 ev it would appear that it cannot be a result of electron hopping on octahedral sites. It is suggested then, that the room temperature conductivity of our deposits is due to electron exchange between Fe^{2+} and Fe^{3+} ions on octahedral sites with an activation energy of 0.115 ev. There may be an additional conduction mechanism associated with Fe^{2+} which has an activation energy of ~ 0.8 ev as evidenced by Kato's measurements on high resistivity material and the optical data on lithium ferrite. The optical data on other materials suggests that the 1.5μ absorption may be due to a transition between tetrahedral Fe^{2+} levels but there is the alternate possibility that it results from electron hopping on the tetrahedral sites or from tetrahedral to octahedral sites.

Domain Patterns.--As discussed in the last interim report and in other publications (Ref. 8, 9) the crystallographic anisotropy in epitaxial magnetic oxide films can be dominated by the magnetostrictive contribution. This leads to easy directions and resulting domain patterns not observed in bulk

specimens. In order to ascertain the extent of the magnetostrictive influence on the anisotropy of our deposits we have extended the calculations to the case of $\{111\}$ LiFe_5O_8 on MgO . This leads to an anisotropy field along the $\langle 111 \rangle$ given by

$$H_A\langle 111 \rangle = -\frac{4K_1}{3M_s} - \frac{7\lambda_{111}\sigma}{3M_s} = H_K\langle 111 \rangle + H_\sigma\langle 111 \rangle$$

where σ is the thermally induced mechanical stress resulting from the thermal expansion mismatch between film and substrate. This stress is given, under certain assumptions (Ref. 9) by $\sigma = \frac{Y}{1-\mu} \Delta\alpha\Delta T$

Here Y and μ are Young's modulus and the Poisson ratio of the deposit, $\Delta\alpha$ is the difference in expansion coefficient of film and substrate and ΔT is the difference between deposition and room temperatures.

Since lithium ferrite undergoes a phase transition at $\sim 750^\circ\text{C}$ the calculation of σ for $\text{LiFe}_5\text{O}_8/\text{MgO}$ is more complicated than in the case of YIG/YAG. However using

$$\begin{aligned} \Delta\alpha &= +2 & T > 750^\circ\text{C} \\ \Delta\alpha &= -1.7 & T < 750^\circ\text{C} \end{aligned} \quad (\text{Ref. 10, 11})$$

and typical values of $Y = 2 \times 10^{12}$, $\mu = 0.25$, $\Delta T = 900^\circ\text{C}$

we obtain $\sigma = -2.3 \times 10^9$ dynes/cm² where $\sigma < 0$ denotes film compression.

Using literature values of $H_K\langle 111 \rangle = +550$ (Ref. 12) and $\lambda_{111} = -3 \times 10^{-6}$ (Ref. 13)

gives $H_A\langle 111 \rangle = +550 - 50 \approx +500$ Oe. Thus, for $\{111\}$ deposits on MgO

the crystallographic anisotropy dominates and the easy direction should lie along $\langle 111 \rangle$, i.e. normal to the film plane. Demagnetizing effects would

tend to produce closure domains in the plane of the films but one would still expect to be able to see a pattern by either the Faraday or Bitter techniques. The only explanation for the failure to observe domain patterns in the films is that their size is below our limit of resolution. The roughness of the surfaces limits the useful magnification under which the films can be examined.

Ferromagnetic Resonance.--The X-band microwave absorption spectra have been obtained for several deposits. The observed linewidths have been very broad, on the order of 200-600 Oersteds. The lines in \perp resonance ($H_{DC} \perp$ film plane) are considerably asymmetric with the relaxation times shorter on the low field side of the peak than on the high field side. This indicates that imperfection scattering to degenerate spin waves is a significant loss mechanism in the deposits. With lines this broad in thin films part of the high field side of the main resonance line can lie outside of the magnon manifold. This results in an abrupt decrease in relaxation time as the density of degenerate spin wave states is reduced to zero. However, in deposits containing Fe^{2+} , ΔH will be large even in the absence of imperfection scattering. In view of the fact that many of the deposits have contained Fe^{2+} and/or precipitated second phases, the broad linewidths are not surprising. In order to obtain ΔH values approaching one Oersted it will be necessary to achieve stoichiometric, smooth, single phase deposits of good crystal quality.

Presently the FMR measurements are used mainly to gain further insight into the nature of the deposits. The dual nature of films such as 262Z1 is detectable by the resonance measurements. In the spectrum of 263Z1 two

distinct lines are observed. The sample geometry and the microwave power level were such that the second line could not be a subsidiary absorption or a magnetostatic mode. The decrease in magnetization upon anneal is observed as a reduction in the applied DC field for μ resonance. The separation into two phases produced by annealing has also been observed in certain samples. The spectrum of deposit 379Z2 consisted of a single line prior to anneal but showed two separate lines after anneal.

Magnetoelastic devices.--The attempt at phonon generation with Sample 376Z1.5 after anneal was again unsuccessful. The probable cause for this lack of success is that the linewidth even after anneal is quite broad. This is probably due to imperfection scattering from tiny precipitates of α -Fe₂O₃.

Presently work is being done on the investigation of magnetoelastic interaction of surface and volume waves in epitaxial YIG films (Ref. 14, 15, 16). Some recent experiments have yielded results showing magnetoelastic conversion is possible when a meander line coupler of the proper configuration is used which efficiently inserts r-f energy. This same work can be extended to LiFe₅O₈ with definite advantages if material can be synthesized with a linewidth value ΔH in the 2 Oe or smaller range. These values of ΔH are attainable, based on the reported value of 1.4 Oe for bulk LiFe₅O₈ (Ref. 12).

The advantages of using LiFe₅O₈ over YIG for this application are twofold:

1. The magnetoelastic constant B_1 for LiFe₅O₈ is 70×10^{-6} ergs/cm³ compared to a B_2 of 7×10^{-6} ergs/cm³ for YIG. Consequently a tenfold stronger effect is expected in LiFe₅O₈.

2. The shear acoustic velocity of LiFe_5O_8 is smaller than in the MgO substrate, whereas in the YIG on GdGaG epitaxial configuration the opposite is true. From the point of view of acoustic propagation this is highly desirable since the acoustic wave is then better confined to the epitaxial layer and the acoustic losses are reduced. The combination of LiFe_5O_8 on MgAl_2O_4 would be even better in this respect.

TECHNICAL ANALYSIS

Depositions

On the basis of thermodynamic considerations of reactivity the replacement of FeCl_2 with FeCl_3 as the iron source material seemed highly desirable. However, we have not been able to experimentally attain this apparent advantage. The main problem has been the lack of reproducibility in the reactivity and the transport rates of FeCl_3 . The best deposits with the ferric material initially looked quite promising in terms of slower growth rates and smooth surfaces. Further evaluation, however, showed that they were high in iron and low in magnetization similar to earlier deposits made with FeCl_2 . Consequently, the decision has been made to return to the FeCl_2 -LiI system and to make small excursions about the deposition conditions which have produced the films closest to stoichiometric LiFe_5O_8 .

The extension of the calculations of Wehmeier (Ref. 3) to the CVD process is underway. These results should provide a means of qualitatively predicting which deposition changes will produce equivalent effects in the growth process. The process of optimizing the growth conditions should then be considerably accelerated.

Characterization

The evaluation of low magnetization deposits has shown that the mechanism responsible for the observed moment is not the same in all cases. Low values of film moment can result from a two layer deposit in which one layer has a high value of $4\pi M_s$ and the other layer is only weakly magnetic

or non-magnetic. Single layer films which have low magnetization can result from various combinations of separate phases with different magnetizations.

Although the low room temperature resistivity of the films and the 1.5μ optical absorption band both result from the presence of Fe^{2+} it appears that they are produced by somewhat different mechanisms. The 0.115 eV activation energy for conduction leads to the assignment of Fe^{2+} - Fe^{3+} electron exchange between octahedral sites as the dominant source of room temperature conductivity in Sample 379Z1.5. The 1.5μ band corresponds to a much higher energy (~ 0.8 eV) and may result from electron exchange between other than octahedral sites or from a level transition in tetrahedrally coordinated Fe^{2+} .

The ferromagnetic resonance characteristics of the deposits suggest that both Fe^{2+} - Fe^{3+} valence exchange and imperfection scattering contribute to the large values of observed linewidth. The X-band FMR spectra are useful in detecting two-component deposits and in studying the effect of anneal on the film magnetization and composition.

The deposits made with FeCl_3 showed certain desirable features such as higher resistivity but the low $4\pi M_s$ and the high iron content show that the problem of reactivity imbalance has not been eliminated as hoped. It would appear that the FeCl_3 has also drastically affected the LiI reactivity to the point where it is less than that of the iron compound.

The incentive to achieve high quality epitaxial thin films of Li ferrite has been given greater impetus by certain device studies in area of

surface acoustic waves. It appears that, if bulk quality can be attained or surpassed, epitaxial LiFe_5O_8 on MgO or MgAl_2O_4 has certain advantages over YIG on GGG for the excitation and propagation of acoustic waves in the microwave region.

Application of the various analytical methods in the proper sequence usually results in a rather complete identification and characterization of a deposit. It remains an unfortunate fact, however, that a combination of such analyses is required to adequately evaluate any given film. At this time it appears that the ferromagnetic resonance linewidth may be the most sensitive single measurement in determining the stoichiometry and the crystal quality of the lithium ferrite deposits.

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